

養成技術者の研究・研修成果等

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2. 養成カリキュラム名: 石炭の完全脱灰による環境負荷低減技術

3. 養成カリキュラムの達成状況

計画に従って、順調に進んで来た。有機溶剤抽出による灰の分離技術の習得とその機構解明の研究を行い、石炭の溶媒処理並びに得られた生成物の回収技術に関して、世界的レベルの技術を身に付けた。三年間で国際石炭会議 (ICCS) にて 1 回、日中石炭・C1 シンポジウム 1 回など国際学会 4 回でプレゼンテーションを行っており、得られた研究結果はアメリカ化学会 "Energy & Fuels" など国際誌に 6 報発表されている。具体的な分析技術として、ガスクロマトグラフィー (GC)、高速液体クロマトグラフィー (HPLC)、赤外吸収スペクトル (FT-IR)、核磁気共鳴 ($^1\text{H-NMR}$, $^{13}\text{C-NMR}$)、示差走査熱量測定 (DSC)、熱重量分析 (TG) 技術が挙げられ、いずれも本人に測定と解析を任せられるレベルの技術を有した。

4. 成果 (A 4 版 3 枚程度)

Title: Studies on Thermal Extraction with Organic Solvent for Ashless Coal Production

Objectives: A large amount of CO_2 emission by coal in comparison to other fossil fuels is one of the world-widely greatest concerns in coal utilization. In power generation, usage of coal for gas turbine which accompanies the direct combustion is one of the most attractive methods to achieve a high net power output, reduce a large CO_2 emission. In order to success this system without the subsequent treatment of combustion gas and the erosion and corrosion of the blade, mineral matter (ash) in coal must be removed prior to its direct combustion. So far, the production of ashless coal has been attempted by hydrothermal treatment using acid and alkaline. However, the treated coal seems to contain ash by 0.1-0.5%, including 60 ppm of sodium, which may not be a sufficient level for its direct combustion into gas turbine. Recently, the authors are developing the ashless coal by organic solvent extraction under mild conditions with no hydrogen atmosphere. The required extraction yield is more than 60%, and ash content in the ashless coal is less than 0.02% containing less than 0.5 ppm sodium and potassium. Thermal extraction with organic solvent at temperature up to 360°C was effective way to produce ashless coal (HyperCoal) in a high yield for some middle rank coals with lower softening temperature and higher maximum fluidity. While, the extraction yields for low rank coals are still low, and the extraction mechanisms are not clear yet. In this study, the behavior of coal free radicals were investigated directly, using *in situ* EPR spectroscopy at temperatures below 300°C in high polar solvent *N*-methyl-2-pyrrolidinone (NMP) and non-polar solvent 1-methyl-naphthalene (1-MN), which are all used as solvents for producing HyperCoal. At the same time, hydrogen-donating solvents, 1,4,5,8,9,10-hexahydroanthracene (HHA) and mixtures of NMP and HHA were also used as the solvent. Furthermore, the effects of the addition of various inorganic salts (lithium halide: LiCl, LiBr, LiI) on the dissolution of coals in NMP and the effect of acid treatment on the thermal extraction yield for different kinds of coal

were also investigated. At the same time, the mechanisms for the inorganic salts addition, acid treatment and the organic solvent extraction were discussed.

Result1: The Behavior of Free Radicals in Coal at Temperatures up to 300°C in Various Organic Solvents, Using in Situ EPR Spectroscopy

In situ electron paramagnetic resonance (EPR) spectroscopy was used to investigate the behavior of free radicals in the Banko coal (C%: 71.3%) that was heated to 300°C in HHA, NMP, and mixtures of the two solvents (NMP/HHA). As shown in Figure 1, with HHA, the radical intensity increased slightly as temperature increased from 60 to 200°C, and then decreased greatly as it increased to 300°C. In contrast, the radical intensity in NMP increased greatly from 60°C to 260°C and then decreased slightly. When NMP/HHA mixtures were used, the decrease in radical intensity was very dependent on the proportion of HHA. NMP,

which is an aprotic polar solvent, might interact with the free radicals and prevent the radical molecules from coupling and taking part in addition reactions. While, these interactions between NMP and free radicals seem to be unstable; with increasing temperature, these free radicals may become more active, and coupling and addition reactions may occur readily. However, when an NMP/HHA mixture was used, the synergistic effect of NMP and HHA stabilized the free radicals.

Result2: Coal Dissolution by Heat treatment at Temperatures up to 300°C in NMP with Addition of Lithium Halide

Coals of different ranks were heat-treated at temperatures up to 300°C in the aprotic dipolar solvent NMP with addition of lithium halides (LiCl, LiBr, and LiI). As shown in Figure 2, for low-rank Banko 97 coal (%C:70.0%), the dissolution yield (TIMS+TS) was increased by 41.4% at 300°C, from 50.4% in NMP alone to 91.8% with the addition of 2.4 mmol/g-coal LiCl. Furthermore, the temperature of heat treatment (175-300°C) and the quantity of LiCl added (0.6-3.6 mmol/g-coal) markedly affected the dissolution yield.

When different lithium halides were used, the dissolution yield was increased in the order $Cl^- > Br^- > I^-$; higher charge density of the anion of the additive was associated with higher dissolution yield. FT-IR spectrometry was used to investigate structural changes in coals that were heat-treated in NMP with addition of LiCl under various conditions. The

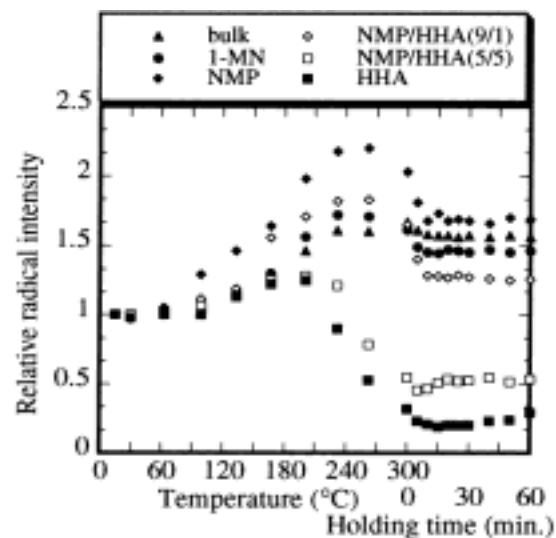


Figure 1. Relative radical intensities of total radicals versus temperature and holding time for Banko coal heat-treated up to 300 °C in various solvents.

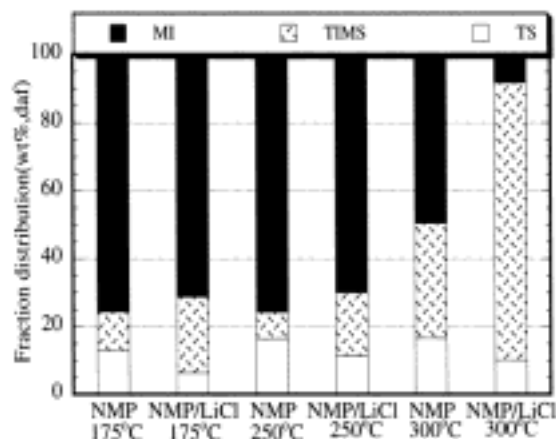


Figure 2. Fraction distribution of Banko 97 coal heat-treated in NMP alone and with the addition of LiCl at 2.4 mmol/g-coal at 175 °C, 250 °C, and 300 °C for 1 h.

intensity of the peak corresponding to carboxylic acid groups in low-rank Banko 97 coal decreased, while the intensities of carboxylate group peaks increased after heat treatment of the coal at 300°C. The mechanism of the effect of the addition of LiCl on the dissolution of low-rank coal is suggested to be as follows. Heat treatment of low-rank coals at 175-300 °C in NMP with the addition of LiCl results in the formation of a complex between lithium and n molecules of NMP with chloride anion, $[\text{Li} \cdot n \text{ NMP}]^+ \text{Cl}^-$. Due to its high basicity, the Cl^- anion releases the aggregation of the coal by weakening the hydrogen bonds formed between carboxyl acid groups, resulting in the observed high dissolution yields.

Results3: Elucidation of Mechanisms Involved in Thermal Extraction during Ashless Coal Production

Thermal extractions of coals with different ranks were carried out under various extraction conditions. The extraction yields increased with increasing the extraction temperature from 200 °C to 360°C using a nonpolar solvent 1-MN or a high polar solvent of NMP as the extraction solvent. At the same temperature, NMP gave much higher extraction yields than 1-MN for some middle and lower rank coals, while, for a high rank Pocahontas No.3 coal, their extraction yields were similar. DSC (differential scanning calorimetry) thermograms showed that the coal aggregates for some middle and lower rank coals were greatly relaxed by NMP addition, while were not affected by 1-MN addition. In contrast, for Pocahontas No.3 coal, the relaxation of coal aggregates did not occur by either 1-MN or NMP addition. Heat/solvent-induced relaxation of coal aggregates by NMP may result in the high extraction yields for some middle and lower rank coals. While, for some low-rank coals, i.e., Wyodak coal (C%, 75.0%), the extraction yields were very low even extracted in polar solvent NMP.

Some low-rank coals, i.e., Wyodak coal, as shown in Figure 3, acid-treated in HCl, aqueous methoxyethoxy acetic acid (MEAA) and acetic acid (AA), and then extracted in NMP, showed a considerable increase in thermal extraction yield at 360°C, as the acid concentration increased from 0.01 to 0.1 M. No significant changes were seen with a further increase in acid concentration to 1.0 M. A corresponding decrease occurred in the intensity of FT-IR spectral bands near 1,555 and 1,400 cm^{-1} , assigned to metal carboxylate groups, as acid concentrations increased from 0.01 to 0.1 M, while bands assigned to carboxyl groups at about 1,720 cm^{-1} increased over the same range. Furthermore, most Mg^{2+} and Ca^{2+} ions could be

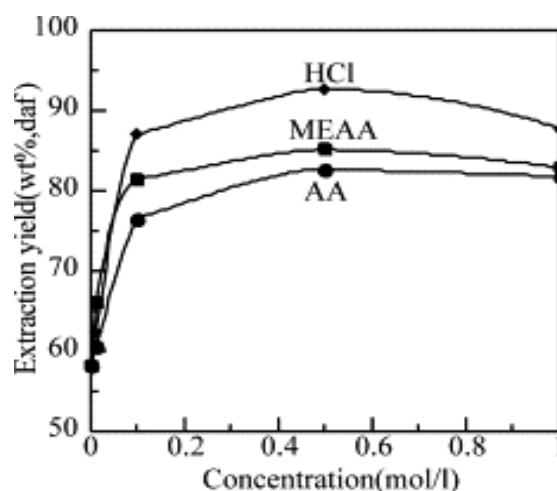


Figure 3. Extraction yields with NMP at 360 °C for 60 min, for acid-treated WY in MEAA, AA, and HCl at different concentrations.

removed from the coals with acids between 0.01 and 0.1 M. Thermogravimetric analyses showed that the acid-treated coal yielded a similar weight loss to that of raw coal. Hence thermal decomposition of acid-treated coals cannot play a significant role in the increase in extraction yield that is obtained with polar solvents. As shown in Figure 4, a mechanism is proposed for the processes involved in the acid treatment and thermal extraction of some low-rank coals: cation-bridging cross-links existing among metal carboxylate groups in the low-rank raw coals are released upon removal of Mg^{2+} and Ca^{2+} ions by acid treatment. The resulting carboxyl groups then form new hydrogen bonds among themselves,

which can become released when polar NMP solvent is introduced. Thus, both the structural relaxation of cation-bridging cross-links by acid treatment and the release of the hydrogen bonds by NMP are involved in the enhancement of extraction yields upon acid-treatment of some low-rank coals.

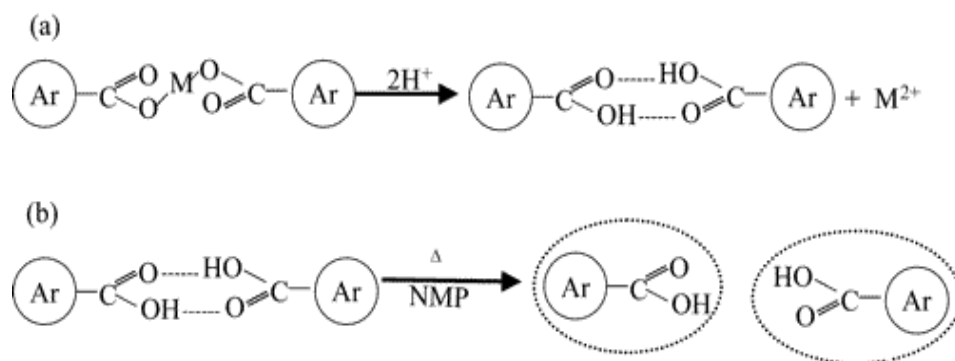


Figure 4. Proposed contrasting mechanisms for the acid treatment (a), and thermal extraction of coal with NMP (b).

5 . 成果の対外的発表等

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(2) 口頭発表 (発表済を対象。)

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(3) 特許等 (出願番号を記載)

なし